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EMISSION CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS AND VOLATILE ORGANICS IN THE VENT GAS OF A MOBILE PCB DESTRUCTION FACILITY

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An emission testing program has been carried out to determine the concentrations of PCB and 14 volatile organic compounds in the vent gas of a Mobile PCB Destruction Unit (MPU-1) during the processing of an oil mixture in storage at the Ontario Hydro Research Division site. The discovery of a fine mist of oil in the vent gas system during the operation of the unit has somewhat jeopardized the success of the test program. Its presence adversely affected the collection efficiency of the adsorption tubes used to sample some of the compounds and caused a rapid deterioration in the performance of the emission control device. This oil mist must be eliminated before the normal emissions from the process can be measured. Regardless of the above problem, only seven of the 15 compounds specified for testing by the Ontario Ministry of the Environment were detected in the vent gas. The detection of these compounds can be attributed directly to their presence in the feed oil, and therefore the oil mist in the vent gas. This oil stock was rather unique in that is consisted of a complex mixture of insulating and lubricating oils plus a variety of solvents and other volatile organic compounds. Benzene was found at the highest concentrations because it is a product of the dechlorination process. The feed oil was found to contain sufficient quantities of various chlorinated benzenes to account for the emitted benzene. PCB (in this case, Aroclor 1260) emissions were the lowest at less than 2000 ng/m3, and would probably be even lower in the absence of the oil mist in the vent gas system.

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1.0 INTRODUCTION

The rationale and methodology used for sampling the emissions from Ontario Hydro's Mobile PCB Destruction Unit (MPU-1) have been documented previously /1/. Basically, the Ontario Ministry of the Environment (MOE) required that the concentrations of the following compounds be measured in the MPU-1 vent gas both upstream and downstream of the emission control device /2/:

Benzene	
Toluene	
PCB	
Vinyl chloride	(Chloroethylene)
Vinylidene chloride	(1,1-Dichloroethylene)
trans-1,2-Dichloroethane	(trans-1,2-Dichloroethylene)
Trichloroethylene	
Tetrachloroethylene	
Methyl chloride	(Chloromethane)
Methylene chloride	(Dichloromethane)
Chloroform	(Trichloromethane)
Carbon tetrachloride	(Tetrachloromethane)
Ethylene chloride	(1,2-Dichloroethane)
Methyl chloroform	(1,1,1-Trichloroethane)
1,2-Dichloropropane	

The alternative compound names shown in brackets are given for information only, except for trans-1,2-dichloroethylene. This is in fact the correct compound sought, rather than the MOE specified trans-1,2-dichloroethane. The latter does not exist because of free rotation around single carbon-carbon bonds.

The following emission results have been derived from two data sets that are reported separately. These reports include the sample collection results such as volumes of vent gas sampled /1/, and the results for the analyses of the feed oils and collected samples /3/. In addition to emission concentrations for all of the above listed compounds, removal efficiencies for the control device (two carbon filters in series) have been calculated where possible and a mass balance has been attempted for those compounds found above their detection limits in the vent gas.

2.0 RESULTS AND DISCUSSION

2.1 MPU-1 Operating Data

Table I gives some of the MPU-1 operating data recorded during the test program. Six tests were run, three during the filling stage and three

during the processing stage of the PCB destruction process, representing the treatment of three complete batches of oil. Four samples were collected and analyzed for each test, a control device inlet and outlet sample for PCB and the same for volatile organic compounds.

TABLE I

Operating Data for the MPU-1 and the Vent Gas Sampling System During Testing of the Emissions

	Emission Test Number					
	1	2	3	4	5	6
Date	Dec 15	Dec 15	Dec 16	Dec 16	Dec 17	Dec 17
Activity	Fill	Process	Fill	Process	Fill	Process
Volume of oil (L)	1576	-	1441	-	1510	-
PCB content (mg/kg)	3040	-	3000	-	2700	-
Volume of vent gas emitted (m3)	9.35	1.08	13.62	1.01	9.26	1.20
Volume of vent gas sampled (L)						
PCB :						
Inlet	5.20	8.66	8.74	6.88	5.47	3.34
Outlet	3.76	6.28	6.34	4.98	4.00	2.42
Organics :						
Inlet	4.14	6.90	6.97	5.48	4.36	2.67
Outlet	3.76	6.28	6.34	4.98	4.00	2.42

2.2 Emission Concentrations

Of the 15 compounds sought, only seven were detected in the MPU-1 vent gas at either the control device inlet or outlet. The results for each one of these will be discussed individually below. The detection limits for the emissions of the other eight compounds (vinyl chloride, vinylidene chloride, trans-1,2-dichloroethylene, methyl chloride, methylene chloride,

carbon tetrachloride, ethylene chloride and 1,2-dichloropropane) are listed in Tables A1 to A8, respectively, in Appendix A.

2.2.1 Benzene

Benzene was found at the highest concentrations of all the compounds measured. Its emissions are shown in Table II.

TABLE II

Concentrations of Benzene in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	1450	600
2	Processing	> 5160	1450
3	Filling	440	830
4	Processing	> 5850	4020
5	Filling	860	1220
6	Processing	> 12400	> 12600

There are several points to be made regarding these data that are also generally applicable to the results for the other volatile organics.

Some of these results are reported as "greater than" values. The analytical results for these samples showed that significant quantities of the analyte had been trapped in all four sections of the sample collection device (two adsorption tubes in series, each with a front and back section). This indicates that sample collection was not quantitative and an unknown portion of the total emissions had not been sampled. Such results are therefore invalid and can be used for information only. This generally occurred only for the samples collected at the inlet to the control device during the processing stage, when the highest concentrations were encountered.

Concentrations at both the inlet to and the outlet from the control device were highest during the processing stage. This was probably because the vent gas flow was much higher during the filling stage (see Table I for total volumes emitted during each test), and was comprised of mainly dilution air and/or nitrogen.

The performance of the control device deteriorated significantly as the number of tests run increased. In fact, except for Test Numbers 1, 2 and 4, higher concentrations were found at its outlet than at the inlet. This strongly suggests that the carbon filters were merely delaying the emissions, rather than removing them. It should be noted that new charcoal filters had been installed prior to the test program. Consequently, only Test No 1 and perhaps Test No 2 with removal efficiencies of about 60% or better can be considered typical of their performance.

The most likely explanation for the failure of the control device is saturation of the charcoal by a fine oil mist that was discovered in the vent gas upstream of the filters. This would also explain the poor collection efficiency of some of the sample collection tubes (also containing activated charcoal) used at the control device inlet. Modifications to the vent gas system to eliminate this mist before it reaches the control device are necessary before the emissions can be reduced.

2.2.2 Toluene

The results for toluene emissions are shown in Table III. In general, they follow trends similar to those for benzene.

TABLE III

Concentrations of Toluene in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	300	42
2	Processing	500	170
3	Filling	360	140
4	Processing	410	340
5	Filling	200	180
6	Processing	640	1040

Again, concentrations during processing were higher than during filling. No "greater than" values were recorded and the control device performance was better than for benzene, with a higher outlet concentration not being observed until the final test. This suggests that the effect of the oil

mist on the activated charcoal filters and adsorption tubes was less pronounced for toluene. It could also be due to the lower absolute amounts of this compound in the vent gas.

2.2.3 Polychlorinated Biphenyls

The emission concentrations of PCB are shown in Table IV. Note that these results are in ng/m3, rather than mg/m3 which has been used for the volatile organics.

TABLE IV

Concentrations of Polychlorinated Biphenyls in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (ng/m3)	Control Device Outlet (ng/m3)
1	Filling	1670	< 1330
2	Processing	< 580	< 800
3	Filling	1640	900
4	Processing	< 730	< 1000
5	Filling	1590	< 1250
6	Processing	1650	< 2070

In contrast to the volatile organic results, concentrations of PCB were generally found to be lower during the processing stages than during the filling stages. This demonstrates the absence of any significant PCB losses during the actual dechlorination process. It also shows that components of the feed oil such as PCB are carried through the vent gas system during filling, probably in the fine oil mist mentioned earlier.

Unfortunately, the requested detection limit of 450 ng/m3 could not be met for most samples. This was the result of failure to collect the maximum allowed sample volume /1/ and lower than expected recovery of the PCB from the adsorption tubes /3/. Consequently, not a lot can be said about the performance of the control device other than it appears that the PCB was more effectively retained than the other, more volatile organic compounds.

It is interesting to note the relative consistency of the PCB levels at the control device inlet during each of the filling stage tests. This indicates that the carry-over of feed oil components as an oil mist was a reasonably

constant phenomenon for this batch of oil. It also shows the ability of the Florisil adsorption tubes to trap PCB even in the presence of this mist.

2.2.4 Trichloroethylene

As shown in Table V, traces of trichloroethylene were found in all the samples. Only one of the results had to be reported as a "greater than" number because of a poor collection pattern in the adsorption tubes. The trends of higher concentrations during processing and decreased control device performance with increasing time of operation were also observed at these low concentrations.

TABLE V

Concentrations of Trichloroethylene in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	0.81	0.45
2	Processing	> 2	0.75
3	Filling	0.92	0.54
4	Processing	1.6	1.3
5	Filling	0.46	0.45
6	Processing	2.4	3.6

2.2.5 Tetrachloroethylene

The concentrations of tetrachloroethylene found were extremely similar to those for toluene, as were the trends in the data.

TABLE VI

Concentrations of Tetrachloroethylene in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	290	40
2	Processing	570	140
3	Filling	370	140
4	Processing	490	300
5	Filling	220	180
6	Processing	820	1030

2.2.6 Chloroform

Small amounts of chloroform were found in the samples. Unfortunately, four of the results are reported as "greater than" values because of poor sample collection efficiencies. This tends to contradict the possibility that better control device and sample tube performance for some other compounds was related to their relatively low concentrations compared to benzene (see Section 2.2.2). It is probably more related to the lower volatilities of these compounds.

TABLE VII

Concentrations of Chloroform in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	2.2	1.3
2	Processing	> 0.6	4.6
3	Filling	1.3	1.1
4	Processing	> 0.8	2.5

5	Filling	0.6	0.7
6	Processing	> 1.7	> 1.3

2.2.7 Methyl Chloroform

The emissions of methyl chloroform (1,1,1-trichloroethane) are shown in Table VIII. The concentrations were relatively high, compared to the other chlorinated paraffins such as chloroform. The trends of higher concentrations during the processing stage and decreased performance of the control device were again evident.

TABLE VIII

Concentrations of Methyl Chloroform in the Vent Gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	9.7	5.9
2	Processing	> 10	11
3	Filling	17	13
4	Processing	> 10	29
5	Filling	6.7	7.0
6	Processing	> 17	47

2.3 Performance of the Emission Control Device

The performance of the control device for each of the detected compounds has already been discussed in Sections 2.2.1 to 2.2.7. These results are summarized in Table IX to allow a more convenient view of the data.

Even in the absence of a complete set of data, the following observations can be made regarding the performance of the control device;

PCB, the least volatile species of the compounds detected, was partially removed and retained by the carbon filters throughout the duration of the tests. There was no evidence that it was eluted from the charcoal with time of operation.

Significant portions (40% to 85%) of all the detected volatile organics were removed during the first and probably the second tests. Fresh charcoal filters had been installed prior to the test program.

The performance of the control device deteriorated rapidly after the first two tests, to the extent that eventually more material was being eluted from the filters than was entering them. This was most likely due to saturation of the charcoal by the previously mentioned fine oil mist in the vent gas. Consequently, only the data for the first two tests can be used to judge the normal removal efficiencies for the various compounds.

The behavior of benzene, found at the highest concentration of the compounds detected, was somewhat unique. The data suggest that once the carbon filters had been contaminated by the oil mist, benzene was loaded onto them during the relatively low flow rate processing stage but was then eluted off again during the high flow rate filling process. It is not clear if this effect would be observed in the absence of the oil mist contamination.

TABLE IX

Efficiency of the MPU-1 Control Device for Removing Various Compounds in the Vent Gas Stream

	Removal Efficiency Found During Test No					
	1	2	3	4	5	6
	Fill	Process	Fill	Process	Fill	Process
PCB	> 20%	*	45%	*	> 21%	*
Benzene	59%	> 72%	- 90%	> 31%	- 42%	*
Toluene	86%	66%	61%	17%	10%	- 62%
Trichloro -ethylene	44%	> 63%	41%	19%	2%	- 50%
Tetrachloro -ethylene	86%	75%	62%	39%	18%	- 26%
Chloroform	41%	*	15%	*	- 17%	*
Methyl chloroform	39%	*	24%	*	- 5%	*

NOTES:

A negative efficiency indicates that the outlet concentration was greater than that in the inlet.

A "greater than" efficiency indicates that either the inlet concentration was recorded as a "greater than" value or the outlet concentration was a "less than" value.

A "*" symbol indicates that no efficiency could be calculated for that data pair. Examples of this include a pair of "greater than" values, a pair of "less than" values, or a "greater than" inlet concentration that was numerically smaller than a measured outlet concentration.

2.4 Analysis of Samples of the Feed Oil used in the Test Program

It was expected that some PCB would be found in the vent gas because of its known presence in the feed oil at about 3000 mg/kg. Benzene was also expected because it is a product of the dechlorination of chlorinated benzenes that are often found in these oils. However, the discovery of the other five volatile organics was somewhat surprising, especially during the filling stage of the process. Consequently, three samples of the feed oil were analyzed for these compounds. One sample had been degassed during the filling stage of the MPU-1 operation. The other two were the same oil, but taken directly from the holding tank. The results of these analyses are given in Table X. Results for PCB and the various chlorinated benzenes are included, the latter being the main source of the benzene emissions.

All of the detected compounds were found in the feed oil. In addition, the five that were not expected were found in concentration ratios that closely paralleled the ratios of their emission concentrations in vent gas at the control device inlet. This clearly shows that they were not products of the dechlorination process but were simply carried into the vent gas system in the fine mist of the feed oil. Elimination of this oil mist would therefore also eliminate these emissions.

By contrast, the relatively low levels of benzene in the feed oil show that it is indeed a product of the process. Various chlorinated benzenes were found at concentrations high enough to easily account for the measured benzene emissions. It is interesting to note that the degassed oil sample contained only a small fraction of the benzene found in the untreated feed oil. This indicates that the benzene originally present is released by the degassing treatment during the filling stage.

TABLE X

Analysis of the Feed Oil Used During the Emission Testing of MPU-1

	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)
PCB (Aroclor 1260)	3120	3160	3220
Trichlorobenzene	1160	1250	1215
Tetrachlorobenzene	770	800	790
Pentachlorobenzene	150	150	160
Hexachlorobenzene	41	46	50
Benzene	1.45	1.63	0.04
Toluene	2.75	2.62	2.12
Trichloroethylene	0.019	0.019	< 0.017
Tetrachloroethylene	4.82	4.65	4.22
Chloroform	0.017	0.018	< 0.017
Methyl chloroform	0.95	0.99	0.78

NOTES:

Sample 1 - Oil sampled from near the surface of the holding tank.

Sample 2 - Oil sampled from 2 feet below the surface of the holding tank.

Sample 3 - Sample of degassed oil, taken after it had been pumped from the holding tank into the MPU-1 and was ready for processing.

2.5 Mass Balances for Detected Volatile Organic Compounds

Having established the presence in the feed oil of all of the compounds found in the vent gas, a mass balance was performed to determine if sufficient quantities were present to account for their emissions. These results are shown in Table XI.

TABLE XI

Quantities of Compounds Found in the Vent Gases at the Inlet to and the Outlet from the MPU-1 Emission Control Device, Compared to the Quantities Originally Present in the Feed Oil

	Batch # 1	Batch # 2	Batch # 3
Benzene :			
Present in oil*	2.4 g	2.2 g	2.3 g
Inlet vent gas	> 19 g	> 12 g	> 23 g
Outlet vent gas	7.2 g	15.4 g	> 26 g
Toluene :			
Present in oil	4.2 g	3.9 g	4.1 g
Inlet vent gas	3.3 g	5.3 g	2.6 g
Outlet vent gas	0.58 g	2.3 g	2.9 g
Trichloroethylene :			
Present in oil	30 mg	27 mg	29 mg
Inlet vent gas	> 10 mg	14.1 mg	7.1 mg
Outlet vent gas	5.0 mg	8.7 mg	8.5 mg
Tetrachloroethylene :			
Present in oil	7.5 g	6.8 g	7.1 g
Inlet vent gas	3.3 g	5.5 g	3.0 g
Outlet vent gas	0.53 g	2.2 g	2.9 g
Chloroform :			
Present in oil	28 mg	25 mg	26 mg
Inlet vent gas	> 22 mg	> 18 mg	> 7.6 mg
Outlet vent gas	17 mg	18 mg	> 8.3 mg
Methyl chloroform :			
Present in oil	1530 mg	1390 mg	1460 mg
Inlet vent gas	> 100 mg	> 240 mg	> 80 mg
Outlet vent gas	67 mg	206 mg	121 mg

*NOTE:

Additional quantities of benzene of 1.3 kg, 1.2 kg and 1.3 kg for batches #1 to #3, respectively, would be available if it is assumed that complete dechlorination of all the chlorobenzenes found in the feed oil occurs.

Quantities present in the oil were calculated from the volume of oil loaded for each batch treated (see Table I) and the average of the analyses shown in Table X. Quantities present in the vent gas for a batch of oil are the sum of the amounts of the compound emitted during a filling stage and a processing stage. Each of these amounts was calculated from the total volume of vent gas emitted (see Table I) and the concentration of the compound in the vent gas during that stage of the process (see Tables II to VIII).

Except for benzene, generally the quantity of each compound present in the feed oil exceeded that found in the inlet vent gas. However, as noted in the table of results, benzene is most likely produced, in amounts far in excess of those emitted, by the dechlorination of the chlorobenzenes present in the oil.

3.0 SUMMARY AND CONCLUSIONS

The discovery of the presence of a fine mist of oil in the vent gas system upstream of the MPU-1 emission control device has somewhat jeopardized the success of the test program. This oil mist had several effects:

It prevented the quantitative collection of some of the volatile organics on activated charcoal adsorption tubes at the inlet to the control device.

Similarly, it saturated the charcoal in the carbon filters (the control device), causing a rapid deterioration in its performance.

Its presence in the vent gas obviously resulted in those compounds initially present in the feed oil, including PCB, to also be found as components of the vent gas emissions.

It is therefore essential that the vent gas system be modified to remove this oil mist before it reaches the control device. This would allow optimum control device performance and most likely eliminate, or at least significantly reduce, the presence of many of the compounds found in the vent gas.

Regardless of the above problems, only seven of the compounds specified by the MOE were detected. In order of decreasing concentration, they were benzene, tetrachloroethylene, toluene, methyl chloroform, trichloroethylene, chloroform and PCB (Aroclor 1260). Except for benzene

and PCB, all were found at emission concentration ratios that closely paralleled their concentration ratios in the feed oil. This demonstrates that their presence was most likely due to the fine mist of the oil that was found in the vent gas system and that they could be eliminated by eliminating the mist.

Benzene was an expected component of the vent gas because it is a product of the dechlorination process. Sufficient quantities of various chlorinated benzenes were found in the feed oil to account for its emissions.

PCB was detected only because special analytical procedures were employed in an attempt to achieve a detection limit of 450 ng/m3. Unfortunately, much lower than expected recoveries of the PCB from the Florisil adsorption tubes resulted in detection limits two to three times higher than this value. However, all the emission concentrations at the outlet from the control device were below 2000 ng/m3 and probably would be even lower in the absence of the oil mist in the vent gas system.

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APPENDIX A

Emission Concentration Detection Limits for Compounds Found Below these Values in the MPU-1 Vent Gas.

TABLE A1

Concentrations of Vinyl Chloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.4	< 0.5
2	Processing	< 0.3	< 0.3
3	Filling	< 0.3	< 0.3
4	Processing	< 0.3	< 0.4
5	Filling	< 0.4	< 0.5
6	Processing	< 0.7	< 0.7

TABLE A2

Concentrations of Vinylidene Chloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.3	< 0.3
2	Processing	< 0.2	< 0.2
3	Filling	< 0.2	< 0.2
4	Processing	< 0.2	< 0.2
5	Filling	< 0.3	< 0.3
6	Processing	< 0.4	< 0.5

TABLE A3

Concentrations of trans 1,2-Dichloroethylene in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.4	< 0.4
2	Processing	< 0.2	< 0.3
3	Filling	< 0.2	< 0.3
4	Processing	< 0.3	< 0.3
5	Filling	< 0.4	< 0.4
6	Processing	< 0.6	< 0.6

TABLE A4

Concentrations of Methyl Chloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.4	< 0.5
2	Processing	< 0.3	< 0.3
3	Filling	< 0.3	< 0.3
4	Processing	< 0.3	< 0.4
5	Filling	< 0.4	< 0.5
6	Processing	< 0.7	< 0.7

TABLE A5

Concentrations of Methylene Chloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.3	< 0.4
2	Processing	< 0.2	< 0.2
3	Filling	< 0.2	< 0.2
4	Processing	< 0.3	< 0.3
5	Filling	< 0.3	< 0.3
6	Processing	< 0.5	< 0.5

TABLE A6

Concentrations of Carbon Tetrachloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.3	< 0.3
2	Processing	< 0.2	< 0.2
3	Filling	< 0.2	< 0.2
4	Processing	< 0.2	< 0.2
5	Filling	< 0.3	< 0.3
6	Processing	< 0.4	< 0.5

TABLE A7

Concentrations of Ethylene Chloride in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 1.4	< 1.5
2	Processing	< 0.9	< 1.0
3	Filling	< 0.9	< 1.0
4	Processing	< 1.1	< 1.2
5	Filling	< 1.3	< 1.5
6	Processing	< 2.2	< 2.4

TABLE A8

Concentrations of 1,2- Dichloropropane in the Vent gases of the Mobile PCB Destruction Unit MPU-1.

Test No	Activity	Control Device Inlet (mg/m3)	Control Device Outlet (mg/m3)
1	Filling	< 0.3	< 0.3
2	Processing	< 0.2	< 0.2
3	Filling	< 0.2	< 0.2
4	Processing	< 0.2	< 0.3
5	Filling	< 0.3	< 0.3
6	Processing	< 0.4	< 0.5